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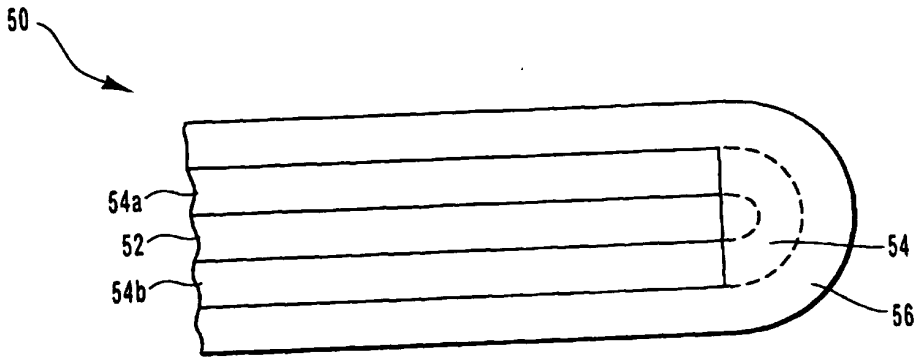

(57) Abstract: Interference pigment flakes and foils are provided which have luminescent and color-shifting properties. The pigment flakes can have a symmetrical coating structure on opposing sides of a core layer, can have an asymmetrical coating structure with all of the layers on one side of the core layer, or can be formed with encapsulating coating around the core layer. The coating structure of the flakes and foils includes a core layer, a dielectric layer overlying the core layer, and an absorber layer overlying the dielectric layer. A luminescent material is incorporated into the flakes or foils as a separate layer or as least part of one or more of the other layers. The pigment flakes and foils exhibit a discrete color shift so as to have a first color at a first angle of incident light or viewing and a second color different from the first color and a second angle of incident light or viewing. The pigment flakes can be interspersed into liquid media such as paints or inks to produce colorant materials for subsequent application to objects or papers. The foils can be laminated to various objects or can be formed on a carrier substrate.

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LUMINESCENT PIGMENTS AND FOILS WITH COLOR-SHIFTING PROPERTIES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to luminescent color-shifting pigments and foils. More particularly, the present invention relates to multilayer color-shifting pigment flakes and foils which have luminescent materials incorporated therein.

2. Background Technology

Various color-shifting pigments, colorants, and foils have been developed for a wide variety of applications. For example, color-shifting pigments have been used in applications such as cosmetics, inks, coating materials, ornaments, ceramics, automobile paints, anti-counterfeiting hot stamps and anti-counterfeiting inks for security documents and currency. Such pigments, colorants, and foils exhibit the property of changing color upon variation of the angle of incident light, or as the viewing angle of the observer is shifted.

The color-shifting properties of the pigments and foils can be controlled through proper design of the optical thin films or orientation of the molecular species used to form the flake or foil coating structure. Desired effects can be achieved through the variation of parameters such as thickness of the layers forming the flakes and foils and the index of refraction of each layer. The changes in perceived color which occur for different viewing angles or angles of incident light are a result of a combination of selective absorption of the materials comprising the layers and wavelength dependent interference effects. The interference effects, which arise from the superposition of light waves that have undergone multiple reflections, are responsible for the shifts in color perceived with different angles. The reflection maxima changes in position and intensity, as the viewing angle changes, due to the absorption characteristics of a material which are selectively enhanced at particular wavelengths from the interference phenomena.

Various approaches have been used to achieve such color-shifting effects. For example, small multilayer flakes, typically composed of multiple layers of thin films, are dispersed throughout a medium such as paint or ink that may then be subsequently applied to the surface of an object. Such flakes may optionally be overcoated to

achieve desired colors and optical effects. Another approach is to encapsulate small metallic or silicatic substrates with varying layers and then disperse the encapsulated substrates throughout a medium such as paint or ink. Additionally, foils composed of multiple layers of thin films on a substrate material have been made.

One manner of producing a multilayer thin film structure is by forming it on a flexible web material with a release layer thereon. The various layers are deposited on the web by methods well known in the art of forming thin coating structures, such as PVD, sputtering, or the like. The multilayer thin film structure is then removed from the web material as thin film color-shifting flakes, which can be added to a polymeric medium such as various pigment vehicles for use as an ink or paint. In addition to the color-shifting flakes, additives can be added to the inks or paints to obtain desired color-shifting results.

Color-shifting pigments or foils are formed from a multilayer thin film structure that includes the same basic layers. These include an absorber layer(s), a dielectric layer(s), and optionally a reflector layer, in varying layer orders. The coatings can be formed to have a symmetrical multilayer thin film structure, such as:

absorber/dielectric /reflector/dielectric/absorber; or

absorber/dielectric/absorber.

Coatings can also be formed to have an asymmetrical multilayer thin film structure, such as:

absorber/dielectric/reflector.

For example, U.S. Patent No. 5,135,812 to Phillips et al., which is incorporated by reference herein, discloses color-shifting thin film flakes having several different configurations of layers such as transparent dielectric and semi-transparent metallic layered stacks. In U.S. Patent No. 5,278,590 to Phillips et al., which is incorporated by reference herein, a symmetric three layer optical interference coating is disclosed which comprises first and second partially transmitting absorber layers which have essentially the same material and thickness, and a dielectric spacer layer located between the first and second absorber layers.

Color-shifting platelets for use in paints are disclosed in U.S. Patent No. 5,571,624 to Phillips et al., which is incorporated by reference herein. These platelets are formed from a symmetrical multilayer thin film structure in which a first semi-

opaque layer such as chromium is formed on a substrate, with a first dielectric layer formed on the first semi-opaque layer. An opaque reflecting metal layer such as aluminum is formed on the first dielectric layer, followed by a second dielectric layer of the same material and thickness as the first dielectric layer. A second semi-opaque layer of the same material and thickness as the first semi-opaque layer is formed on the second dielectric layer.

As discussed above, there are a wide variety of thin film devices produced today, including many that are used as security devices. Although color-shifting pigments and foils provide properties that make them extremely useful as components of security devices, it is desirable to seek additional levels of security by adding additional features.

In European patent application publication EP 0927749A1 to *Bleikolm et al.* (hereafter "*Bleikolm*") multilayered thin films for security and anti-counterfeiting uses are disclosed. Two or more thin layers are deposited in a film, which is subsequently ground into thin film particles. These particles can be mixed into a coating material or incorporated into a bulk material and are optionally luminescent. Both the sequence of layers and their thicknesses can be used to analyze and identify the particles. *Bleikolm* further discloses the use of the multilayer thin film structure as a tag. Further, the thin film particles can be used in a mixture with color-shifting pigments to provide an ink with increased properties. Nevertheless, the thin film particles do not themselves have color-shifting properties.

European Patent Application Publication EP 0927750A1 to *Rozumek et al.* (hereafter "*Rozumek*") discloses the use of two distinct inorganic chemicals incorporated into particles in a predefined and analytical ratio. The particles can be mixed into a coating material or incorporated into a bulk material. The particles provide both spatial and chemical information for security and anti-counterfeiting applications based on the material of the particles and their physical location in an ink as applied to a surface. In one embodiment, one or both of the particles are luminescent.

Unfortunately, the performance of prior color-shifting/luminescent inks has several drawbacks. For example, when color-shifting flakes are combined with luminescent particles, separation tends to occur. The color-shifting flakes and

luminescent particles also tend to be incompatible with the same ink or coating vehicle, making them difficult to use together. Further, the luminescent particles tend to opacify and dull the color performance of the color-shifting flakes.

Additionally, the simple physical mixing of separate color-shifting and luminescent species does not allow for control of the re-emitted spectrum at differing angles since there is no way to control the optical path within simple physical mixtures. Finally, in the current state of the art, forming a thin film interference coating structure that employs a luminescent material as the dielectric is impractical because the stoichiometry of inorganic luminescent materials is very important and their production usually requires processing at temperatures higher than standard coating temperatures.

Accordingly, there is a need for improved coating structures and methods that avoid the above difficulties in forming luminescent color-shifting compositions.

SUMMARY OF THE INVENTION

A luminescent material is incorporated into the flakes or foils as a separate layer or as at least part of one or more of the other layers. The luminescent material can be a fluorescent material, a phosphorescent material, an electroluminescent material, a chemoluminescent material, a triboluminescent material, or other like materials. Such luminescent materials exhibit a characteristic emission of electromagnetic energy in response to an energy source generally without any substantial rise in temperature.

The luminescent pigment flakes and foils exhibit a discrete color shift so as to have a first color at a first angle of incident light or viewing angle and a second color different from the first color at a second angle of incident light or viewing. The pigment flakes can be interspersed into liquid media such as paints or inks to produce colorant materials for subsequent application to objects or papers. Another embodiment of the invention comprises a mixture of one type of luminescent color-shifting flakes with another type of luminescent and/or non-luminescent color-shifting flakes in a predetermined ratio. The foils can be laminated to various objects or can be formed on a carrier substrate.

The foregoing objects and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned

by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to illustrate the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are not therefore to be considered limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

Figure 1 is a schematic representation of a luminescent color-shifting structure according to the invention;

Figure 2 is a plot demonstrating one position of a luminescent layer relative to electric field intensity in a luminescent color-shifting structure according to the invention;

Figure 3 is a plot demonstrating another position of a luminescent layer relative to electric field intensity in a luminescent color-shifting structure according to the invention;

Figure 4 is a schematic representation of another luminescent color-shifting structure according to the invention;

Figure 5 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 6 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 7 is a schematic representation of another luminescent color-shifting structure according to the invention;

Figure 8 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 9 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 10 is a schematic representation of another luminescent color-shifting structure according to the invention;

Figure 11 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 12 is a schematic representation of another luminescent color-shifting structure according to the invention;

Figure 13 is a schematic representation of yet another luminescent color-shifting structure according to the invention;

Figure 14 is a plot demonstrating characteristic absorption of a luminescent material relative to various angles of incident electromagnetic energy; and

Figure 15 is a plot demonstrating characteristic angle-sensitive emission of a luminescent color-shifting structure according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed generally to luminescent multilayer color-shifting pigments and foils and methods of making the same. The pigment flakes and foils have substantial shifts in chroma and hue with changes in angle of incident light or viewing angle of an observer. Such an optical effect, sometimes known as color-shifting, optical variability, or goniochromaticity, allows a perceived color to vary with the angle of illumination or observation. Accordingly, the pigment flakes and foils exhibit a first color at a first angle of incident light or viewing angle and a second color different from the first color at a second angle of incident light or viewing.

Generally, the luminescent color-shifting pigment flakes of the invention can have a symmetrical coating structure on opposing sides of a core layer, can have an asymmetrical coating structure with all of the layers on one side of the core layer, or can be formed with encapsulating coatings which surround a core layer. The flakes and foils generally have a thin film structure that includes a core layer, a dielectric layer overlying the core layer, and an absorber layer overlying the dielectric layer. Each of these layers in the coating structures of the flakes and foils of the invention will be discussed in further detail hereinafter. A luminescent material is incorporated into one or more of the layers of the flakes or foils, with the one or more layers being partially or completely composed of the luminescent material.

In one embodiment of the invention, one or more of the thin film layers is comprised of a luminescent material having optical properties, such as index of

refraction and extinction coefficient, which contribute to the creation of a color-shifting effect as well as providing luminescent properties to the flake or foil. For example, luminescent materials that are non-absorbing in the visible spectrum could be used as dielectrics whereas absorbing luminescent materials could be used as absorbers, reflectors, or partially absorbing dielectrics such as lossy dielectrics.

Another embodiment of the invention uses a distinct luminescent layer within the multilayer stack. This approach allows for additional control of the optical path of incident light and thereby control of the angles of excitation and refraction. Thus, for example, a distinct luminescent sublayer can be interposed at a certain thickness between two dielectric sublayers. The three sublayers together function as a dielectric layer while the luminescent sublayer provides the luminescence to the flake or foil.

Methods of incorporating luminescent materials and layers in an optical stack of a thin film flake or foil generally include sol-gel methods, use of nanoreactors, organic polymer coating processes, vacuum deposition processes, or hybrid combinations of the above methods.

The luminescent pigment flakes can be interspersed into liquid media such as paints or inks to produce various color-shifting colorant compositions for subsequent application to objects or papers. The luminescent foils can be laminated to various objects or can be formed on a carrier substrate. The present invention also includes a mixture of luminescent color-shifting flakes and non-luminescent color-shifting flakes in a predetermined ratio.

As used herein, the term "luminescent material" refers to any atomic or molecular species or solid-state compound that converts at least part of incident energy into emitted electromagnetic radiation with a characteristic signature. Nonlimiting examples include luminescent materials that exhibit fluorescence, polarization, second harmonic generation, phosphorescence, and the like. These materials can be incorporated into one or more of the layers that make up the flake or foil structure. The luminescent material can be employed in solid solution form in the flake or foil, or can be a solid phase such as a crystalline phosphor material.

The function of the luminescent material is to impart optical stimuli responsive characteristics to the pigment flakes and foils. For example, when the

pigment flakes or foils are illuminated with electromagnetic radiation, bombarded with ionizing particles or radiation, or exposed to other excitation energy sources, the flakes or foils emit ultraviolet, visible or infrared radiation of a characteristic wavelength associated with the luminescent material species, or the optical interference characteristics of the flake. Numerous types of luminescent material species are known to one having ordinary skill in the art of photochemistry and physics, and may produce emission of light through any of the emission processes, such as single-photon emission, multiple photon emission, and the like. Examples of suitable luminescent materials for use in the present invention are described in further detail hereafter.

The non-luminescent layers in the color-shifting flakes and foils of the invention can be formed using conventional thin film deposition techniques, which are well known in the art of forming thin film coating structures. Nonlimiting examples of such thin film deposition techniques include physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma enhanced (PE) variations thereof such as PECVD or downstream PECVD, sputtering, electrolysis deposition, and other deposition methods capable of forming discrete and uniform thin film layers. The luminescent materials can be incorporated into the preformed flake or foil structures by a variety of novel methods which are discussed in further detail hereafter.

The present inventors have discovered that color-shifting pigments and foils having luminescent materials incorporated therein produce surprising results. For example, it is an unexpected result of the invention that the addition of certain luminescent materials to color-shifting pigments does not degrade the performance of the color-shifting pigments. Rather, luminescence becomes a secondary feature of the pigments that functions independently of the color shift. In addition, the luminescence yield is surprisingly much higher for color-shifting pigment flakes having luminescent materials therein than for mixtures of color-shifting pigment flakes and fluorescent particles. This is due to a higher percentage of luminescence material available to light exposure in the luminescent pigment flakes than in the mixture of color-shifting pigments and luminescent particles.

Another surprising result occurs when the luminescent layer thickness allows for a high percentage of excitation wavelength light to pass through to an underlying

layer structure of a pigment flake or foil. The excitation light is reflected from the underlying layer structure back into the luminescent layer allowing the luminescent layer to absorb more energy and thereby increase the luminescence yield. This phenomenon is manifested as a change in luminescence intensity with angle of excitation light, since the reflected excitation light is subject to the same incident angle dependency rules as visible light.

A further novel feature of the present invention is the ease of handling and reliability of the luminescent color-shifting pigments. Conventional mixtures of color-shifting pigments and luminescent particles result in mixtures with a tendency to separate into individual components. Thus, the presence of the luminescent material is more easily detectable and it is more difficult to ensure consistent dispersions. The present invention overcomes these problems because the luminescent material cannot separate from the pigment flakes, ensuring uniform compositions. In addition, when luminescent dyes are incorporated into the color-shifting pigment flakes, there is no deleterious effect on the ability of the color-shifting pigment flakes to be substantially planar when set.

Advantageously, the combined luminescent material and interference layers also make a structural analysis of the pigment flakes more difficult for potential counterfeiters. While the luminescent effects are detectable, the structure that creates the luminescent effects cannot be observed by microscopic techniques. It is thus more difficult to analyze and emulate the pigment flakes. In contrast, mixtures of luminescent particles and color-shifting pigments can be readily studied under a microscope to isolate and identify the luminescent particles.

In one embodiment of the present invention, the luminescent material emits electromagnetic radiation when illuminated with electromagnetic energy containing the excitation wavelengths of the luminescent material. The emission of electromagnetic radiation from the color-shifting pigment or foil is a function of the luminescent material's composition and concentration, the incident energy, the overall design of the thin film stack in the flake or foil, the placement of the luminescent layer(s) within the stack, the angle of incidence, and the wavelength-dependant electric field intensity reaching the luminescent layer.

Referring now to the drawings, wherein like structures are provided with like

reference designations, the drawings only show the structures necessary to understand the present invention. Figure 1 depicts a luminescent color-shifting pigment flake 20 according to one embodiment of the invention. The flake 20 is a five-layer design having a generally symmetrical multilayer thin film structure on opposing sides of a reflector layer 22. Thus, first and second dielectric layers 24a and 24b are disposed respectively on opposing sides of reflector layer 22, and first and second absorber layers 26a and 26b are disposed respectively on each of dielectric layers 24 and 25. It is a feature of the invention that at least one of the above layers is a luminescent material, or includes a luminescent material as a sublayer or dispersed throughout the layer. Thus, the luminescent material can be present in the reflector layer, dielectric layer, or absorber layer, depending on the desired structure and material of the particular pigment. Alternatively, the luminescent material can be selected so as to comprise the entire reflector, dielectric, or absorber layer. Each of these layers in the coating structure of flake 20 is discussed below in greater detail.

Although not illustrated, flake 20 can also include further optical coatings. For example, an outer luminescent coating layer could be formed on flake 20. Such a luminescent coating structure for pigment flakes and foils is disclosed in copending U.S. application Serial No. , filed on November 17, 2000 (Docket No. 13676.161), the disclosure of which is incorporated by reference herein. Thus, a luminescent flake or foil of the invention can include a luminescent material incorporated therein as well as an outer luminescent coating layer. Of course, one skilled in the art will recognize that various other optical coatings can be used as long as they do not excessively interfere with the color-shifting or luminescent properties of the flake or foil.

The reflector layer 22 of flake 20 can be composed of various materials. Presently preferred materials are one or more metals, one or more metal alloys, or combinations thereof, because of their high reflectivity and ease of use, although non-metallic reflective materials could also be used. Nonlimiting examples of suitable metallic materials for the reflector layer include aluminum, silver, copper, gold, platinum, tin, titanium, palladium, nickel, cobalt, rhodium, niobium, chromium, and combinations or alloys thereof. These can be selected based on the color effects desired. The reflector layer can be formed to have a suitable physical thickness of

from about 200 angstroms (Å) to about 10,000 Å, and preferably from about 400 Å to about 700 Å.

The dielectric layers 24a and 24b act as spacers in the thin film stack structure of flake 20. The dielectric layers are formed to have an effective optical thickness for imparting interference color and desired color-shifting properties. The dielectric layers may be optionally clear, or may be selectively absorbing so as to contribute to the color effect of a pigment. The optical thickness is a well known optical parameter defined as the product ηd, where η is the refractive index of the layer and d is the physical thickness of the layer. Typically, the optical thickness of a layer is expressed in terms of a quarter wave optical thickness (QWOT) that is equal to $4\eta d/\lambda$, where λ is the wavelength at which a QWOT condition occurs. The optical thickness of dielectric layers can range from about 2 QWOT at a design wavelength of about 400 nm to about 9 QWOT at a design wavelength of about 700 nm, and preferably 2-6 QWOT at 400-700 nm, depending upon the color shift desired. The dielectric layers typically have a physical thickness of about 100 nm to about 800 nm.

Suitable materials for dielectric layers include those having a "high" index of refraction, defined herein as greater than about 1.65, as well as those have a "low" index of refraction, which is defined herein as about 1.65 or less. Each of the dielectric layers can be formed of a single material or with a variety of material combinations and configurations. For example, the dielectric layers can be formed of only a low index material or only a high index material, a mixture or multiple sublayers of two or more low index materials, a mixture or multiple sublayers of two or more high index materials, or a mixture or multiple sublayers of low index and high index materials. In addition, the dielectric layers can be formed partially or entirely of high/low dielectric optical stacks, which are discussed in further detail below. When a dielectric layer is formed partially with a dielectric optical stack, the remaining portion of the dielectric layer can be formed with a single material or various material combinations and configurations as described above.

Examples of suitable high refractive index materials for the dielectric layer include zinc sulfide (ZnS), zinc oxide (ZnO), zirconium oxide (ZrO_2), titanium dioxide (TiO_2), carbon (C), indium oxide (In_2O_3), indium-tin-oxide (ITO), tantalum pentoxide (Ta2O5), ceric oxide (CeO_2), yttrium oxide (Y_2O_3), europium oxide

(Eu_2O_3), iron oxides such as (II)diiron(III) oxide (Fe_3O_4) and ferric oxide (Fe_2O_3), hafnium nitride (HfN), hafnium carbide (HfC), hafnium oxide (HfO_2), lanthanum oxide (La_2O_3), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), praseodymium oxide (Pr_6O_{11}), samarium oxide (Sm_2O_3), antimony trioxide (Sb_2O_3), silicon carbide (SiC), silicon nitride (Si_3N_4), silicon monoxide (SiO), selenium trioxide (Se_2O_3), tin oxide (SnO_2), tungsten trioxide (WO_3), combinations thereof, and the like.

Suitable low refractive index materials for the dielectric layer include silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), metal fluorides such as magnesium fluoride (MgF_2), aluminum fluoride (AlF_3), cerium fluoride (CeF_3), lanthanum fluoride (LaF_3), sodium aluminum fluorides (e.g., Na_3AlF_6 or $Na_5Al_3F_{14}$), neodymium fluoride (NdF_3), samarium fluoride (SmF_3), barium fluoride (BaF_2), calcium fluoride (CaF_2), lithium fluoride (LiF), combinations thereof, or any other low index material having an index of refraction of about 1.65 or less. For example, organic monomers and polymers can be utilized as low index materials, including dienes or alkenes such as acrylates (e.g., methacrylate), perfluoroalkenes, polytetrafluoroethylene (Teflon), fluorinated ethylene propylene (FEP), combinations thereof, and the like.

It should be appreciated that several of the above-listed dielectric materials are typically present in non-stoichiometric forms, often depending upon the specific method used to deposit the dielectric material as a coating layer, and that the above-listed compound names indicate the approximate stoichiometry. For example, silicon monoxide and silicon dioxide have nominal 1:1 and 1:2 silicon:oxygen ratios, respectively, but the actual silicon:oxygen ratio of a particular dielectric coating layer varies somewhat from these nominal values. Such non-stoichiometric dielectric materials are also within the scope of the present invention.

As mentioned above, the dielectric layers can be formed of high/low dielectric optical stacks, which have alternating layers of low index (L) and high index (H) materials. When a dielectric layer is formed of a high/low dielectric stack, the color shift at angle will depend on the combined refractive index of the layers in the stack. Examples of suitable stack configurations for the dielectric layers include LH, HL, LHL, HLH, HLHL, LHLH, as well as various multiples and combinations thereof. In these stacks, LH, for example, indicates discrete layers of a low index material and a high index material. In an alternative embodiment, the high/low dielectric stacks are

formed with a gradient index of refraction. For example, the stack can be formed with layers having a graded index low-to-high, a graded index high-to-low, a graded index low-to-high-to-low, a graded index high-to-low-to-high, as well as combinations and multiples thereof. The graded index is produced by a gradual variance in the refractive index, such as low-to-high index or high-to-low index, of adjacent layers. The graded index of the layers can be produced by changing gases during deposition or co-depositing two materials (*e.g.*, L and H) in differing proportions. Various high/low optical stacks can be used to enhance color-shifting performance, provide antireflective properties to the dielectric layer, and change the possible color space of the pigments of the invention.

The dielectric layers can each be composed of the same material or a different material, and can have the same or different optical or physical thickness for each layer. It will be appreciated that when the dielectric layers are composed of different materials or have different thicknesses, the flakes exhibit different colors on each side thereof and the resulting mix of flakes in a pigment or paint mixture would show a new color which is the combination of the two colors. The resulting color would be based on additive color theory of the two colors coming from the two sides of the flakes. In a multiplicity of flakes, the resulting color would be the additive sum of the two colors resulting from the random distribution of flakes having different sides oriented toward the observer.

The absorber layers 26a and 26b of flake 20 can be composed of any absorber material having the desired absorption properties, including both selective absorbing materials and nonselective absorbing materials. For example, the absorber layers can be formed of nonselective absorbing metallic materials deposited to a thickness at which the absorber layer is at least partially absorbing, or semi-opaque. Nonlimiting examples of suitable absorber materials include metallic absorbers such as chromium, aluminum, nickel, palladium, platinum, titanium, vanadium, cobalt, iron, tin, tungsten, molybdenum, rhodium, niobium, as well as other absorbers such as carbon, graphite, silicon, germanium, cermet, ferric oxide or other metal oxides, metals mixed in a dielectric matrix, and other substances that are capable of acting as a uniform or selective absorber in the visible spectrum. Various combinations, mixtures, compounds, or alloys of the above absorber materials may be used to form the

absorber layers of flake 20.

Examples of suitable alloys of the above absorber materials include Inconel (Ni-Cr-Fe), and titanium-based alloys, such as titanium mixed with carbon (Ti/C), titanium mixed with tungsten (Ti/W), titanium mixed with niobium (Ti/Nb), and titanium mixed with silicon (Ti/Si), and combinations thereof. Examples of suitable compounds for the absorber layers include titanium-based compounds such as titanium nitride (TiN), titanium oxynitride (TiN_xO_y), titanium carbide (TiC), titanium nitride carbide (TiN_xC_z), titanium oxynitride carbide ($TiN_xO_yC_z$), titanium silicide ($TiSi_2$), titanium boride (TiB_2), and combinations thereof. In the case of TiN_xO_y and $TiN_xO_yC_z$, preferably $x = 0$ to 1, $y = 0$ to 1, and $z = 0$ to 1, where $x + y = 1$ in TiN_xO_y and $x + y + z = 1$ in $TiN_xO_yC_z$. For TiN_xC_z, preferably $x = 0$ to 1 and $z = 0$ to 1, where $x + z = 1$. Alternatively, the absorber layers can be composed of a titanium-based alloy disposed in a matrix of Ti, or can be composed of Ti disposed in a matrix of a titanium-based alloy.

The absorber layers are formed to have a physical thickness in the range from about 30 Å to about 500 Å, and preferably about 100 Å to about 175 Å, depending upon the optical constants of the absorber layer material and the desired peak shift. The absorber layers can each be composed of the same material or a different material, and can have the same or different physical thickness for each layer.

The luminescent material incorporated into flake 20 can be composed of either an organic or inorganic material which has the property of luminescence. In general, luminescence is the emission of electromagnetic radiation, or light, from a material without any associated change in temperature, resulting from such causes as chemical reactions, electron bombardment, electromagnetic radiation, and electric fields. Many luminescent materials are excited by high-energy photons or electrons, absorbing incident electromagnetic radiation in one wavelength range, and emitting electromagnetic radiation in another. Luminescence is typically subdivided into the subcategories of fluorescence and phosphorescence. Fluorescence occurs where a substance emits electromagnetic radiation while absorbing some form of energy, with the emission ceasing abruptly when the input energy ceases. Phosphorescence occurs where a substance emits light following the absorption of energy, with the emission continuing for a relatively long time after the energy input has ceased. Additional

subcategories of luminescence include polarization of the incident electromagnetic radiation, and non-linear optical effects such as second harmonic generation.

The luminescent materials used in the present invention can be excited by various energy sources such as infrared radiation, ultraviolet radiation, visible light, electric fields (electroluminescence), magnetic fields (magnetoluminescence), chemical reaction (chemoluminescence), as well as by mechanical stress (triboluminescence).

Nonlimiting examples of suitable organic luminescent materials include fluorescent dyes such as those in the coumarin class, the xanthane class, the acridine class, and numerous others as known to those skilled in the art. Specific examples include Dansyl, prodene, fluorescene, rhodamine, and the like. A fluorescent dye can also be combined with a liquid crystal polymer for incorporation into the color-shifting pigment flakes or foils. Other suitable luminescent materials that can be used in the present invention include the dyes in U.S. Patent Nos. 4,173,002, 5,329,540, and 5,912,257, the disclosures of which are incorporated by reference herein.

Suitable inorganic luminescent materials for use in the invention include halophosphate phosphors, phosphate phosphors, silicate phosphors, aluminate phosphors, borate phosphors, tungstate phosphors, lanthanide phosphors, and the like.

Other luminescent materials useful in the invention include electroluminescent materials such as ZnS, Mn^{++}, $ZnS:TbF_3$, and pi-conjugated polymers; chemoluminescent materials such as dioxetanes, and acridinium salts; and second harmonic generators such as nitrogen-substituted amine stilbene derivatives, molecular complexes of SbI_3 and sulfur, non-centrosymmetric dye aggregates. The luminescent material may also be composed of solid phase or water-soluble quantum dot particles, such as are disclosed in PCT Publication No. WO 00/29617, the disclosure of which is incorporated by reference herein.

The luminescent material can comprise any of the above luminescent materials singly, or in a variety of combinations. For example, a plurality of different fluorescent materials can be used such that a first fluorescent material absorbs and emits light at one set of wavelengths and a second fluorescent material absorbs and emits light at a another set of wavelengths different from the first fluorescent material. Alternatively, the flake could contain a first luminescent layer, which is

light-excited, and a second luminescent layer, which is composed of an electroluminescent material. One skilled in the art will recognize, in view of the disclosure herein, that a wide variety of luminescent materials and combinations thereof could be combined to create greatly enhanced effects.

When a distinct luminescent layer is formed in the flake structure, the luminescent layer has a thickness of about 50 Å to about 15,000 Å, more preferably from about 50 Å to about 5,000 Å, and most preferably from about 50 Å to about 2500 Å. The aspect ratio of the flake structure with a distinct luminescent layer is preferably greater than about two. The aspect ratio of the flakes is ascertained by taking the ratio of the longest planar dimension of the flakes to the edge thickness dimension of the flakes.

By incorporating the luminescent material within a multilayer thin film structure itself, there is no tendency for the luminescent and color-shifting materials to segregate. In addition, adding the luminescent material inside the flake or foil makes it very difficult to detect the presence of the luminescent material using optical or electron microscopy.

One presently preferred method of fabricating a plurality of luminescent pigment flakes, each of which having the multilayer thin film coating structure of flake 20, is based on conventional web coating techniques used to make optical thin films. Accordingly, an absorber layer is deposited on a web of flexible material such as polyethylene terephthalate (PET) which has an optional release layer thereon. The absorber layer can be formed by a conventional deposition process such as PVD, CVD, PECVD, sputtering, or the like. The above mentioned deposition methods enable the formation of a discrete and uniform layer absorber layer of a desired thickness.

Next, a first dielectric layer, for example, is deposited on the absorber layer to a desired optical thickness by a conventional deposition process. The dielectric layer is formed from a luminescent material or a combination of luminescent and non-luminescent materials. The deposition of the dielectric layer can be accomplished by a vacuum deposition process (*e.g.*, PVD, CVD, PECVD).

The luminescent dielectric layer is exposed to the proper temperature and atmospheric conditions to allow conversion of the luminescent material to the proper

stoichiometry. Alternatively, reactive gases can be introduced into a PVD chamber during deposition to control stoichiometry. For example, monatomic or diatomic oxygen can be used to control oxidation. The vacuum deposition processes have the advantage that they may be used with the high temperature processes required to make materials luminescent. Vacuum deposition also allows for smoothness and thickness control.

The reflector layer is then deposited on the first dielectric layer, taking on the characteristics of the underlying dielectric layer. This is followed by a second dielectric layer being deposited on the reflector layer and preferably having the same optical thickness as the first dielectric layer. The second dielectric layer may or may not include a luminescent material. Finally, a second absorber layer is deposited on the second dielectric layer and preferably has the same physical thickness as the first absorber layer.

Thereafter, the flexible web is removed, either by dissolution in a preselected liquid or by way of a release layer, both of which are well known to those skilled in the art. As a result, a plurality of flakes are fractured out during removal of the web from the multilayer thin film. This method of manufacturing pigment flakes is similar to that more fully described in U.S. Patent No. 5,135,812 to Phillips et al., the disclosure of which is incorporated by reference herein. The pigment flakes can be further fragmented if desired by, for example, grinding the flakes to a desired size using an air grind, such that the pigment flakes have a dimension on any surface thereof ranging from about 2 microns to about 200 microns.

While methods of depositing continuous thin film phosphorescent materials are known, few are broadly suitable for all the multilayer thin film structures disclosed and taught by the instant application. The ideal deposition process to produce highly efficient phosphors must result in crystalline films having exceptionally smooth surfaces necessary for interference phenomena in multilayer films. Specifically, the deposition of thin film phosphors with the necessary degree of crystallinity during the deposition process produces a microstructure that does not replicate the underlying substrate with sufficient regularity to be useful in most interference-based thin film designs. Since the crystalline morphology is not easily controlled, the resultant surface roughness disallows further processing steps required

in thin film interference-based designs. The most successful methods, such as liquid phase epitaxy or molecular beam deposition, only deposit crystalline thin films at extremely slow rates and hence are generally not economically viable for the broadest applications of multilayer thin film structures.

A preferred deposition process that overcomes the deficiencies of prior methods is set forth in copending U.S. application Serial No. 09/532,391, filed on March 22, 2000, the disclosure of which is incorporated by reference herein. This patent teaches the use of thermal evaporation, a high deposition rate economical process, for producing thin film phosphors of high crystallinity with the sufficiently smooth surfaces necessary to function in an optical interference pigment flake or foil. It will be readily apparent to one of ordinary skill in the art of thin film technology that this process can be used to create flakes by depositing the phosphor on a substrate or web material compatible with the deposition and annealing temperature, such as glass, fused silica, or a stainless steel belt. If it is not desirable to coat other layers on the same substrate or web material, then flake-like pigment particles are produced by removal of the thin film from the substrate or web material. The phosphorescent flakes can be easily removed from the substrate or web material by providing therebetween a poorly adhering intermediate coating, such as a water soluble salt or thin layer of metal, which can be dissolved in a weak acid or can cause the flakes to be removed by mechanical deformation of a flexible metal web when used. These phosphorescent pigment flakes may then be coated by subsequent processes such as sol-gel coating, electroplating, or CVD in a fluidized bed. An alternative thin film deposition process applicable to the manufacture of phosphorescent crystalline flakes is disclosed in U.S. Patent No. 6,025,677 to Moss et al., the disclosure of which is incorporated by reference herein.

In an alternative embodiment of a luminescent color-shifting flake 20, an asymmetrical color-shifting flake can be provided which includes a three-layer thin film stack structure with the same layers as on one side of the reflector layer in flake 20 as shown in Figure 1. Accordingly, the asymmetrical color-shifting flake includes a reflector layer, a dielectric layer on the reflector layer, and an absorber layer on the dielectric layer. Each of these layers can be composed of the same materials and have the same thicknesses as described above for the corresponding layers of the above

discussed flake 20. In addition, asymmetrical luminescent color-shifting flakes can be formed by a web coating process such as described above in which the various layers are sequentially deposited on a web material to form a thin film structure, which is subsequently fractured and removed from the web to form a plurality of flakes.

Figures 2 and 3 are graphical representations of a color-shifting multilayered structure 30 of the invention which contains a luminescent layer therein. The multilayered structure 30 includes a reflector layer 32, a first dielectric layer 34, a luminescent layer 36, a second dielectric layer 38, and an absorber layer 40. Although the luminescent layer is illustrated as interposed between the dielectric layers, the luminescent layer can be positioned anywhere in the multilayered structure, so long as its optical characteristics are consistent with those of the other layers in creating a color-shifting structure. Thus, the luminescent layer can optionally act as a dielectric, an absorber, or a reflector, depending on its location and optical characteristics.

Figures 2 and 3 also plot the theoretical electric field intensity 42 relative to the distance an electromagnetic wave travels through a multilayer structure at zero degrees from normal. As illustrated in Figures 2 and 3, the luminescent layer 36 can be positioned anywhere between reflector layer 32 and absorber layer 40. Thus, the luminescent layer can be positioned in the center of the dielectric layers 34, 38 (Figure 2), substantially to one side (Figure 3), or even completely to one side and adjacent to the absorber or reflector layers (not shown). In those instances where luminescent layer 36 is incorporated between dielectric layers 34, 38, the luminescent layer functions as a dielectric and necessarily has dielectric qualities such as transparency over most wavelength ranges. Where luminescent layer 36 is adjacent to either reflector layer 32 or absorber layer 40, luminescent layer 36 can be formed to function as a dielectric, an absorber, or a reflector and have the requisite characteristics for such purposes. In this way, the optical distance traveled by wavelengths incident upon and emitted from the luminescent layer 36 can be effectively controlled. As illustrated in Figure 3, when the luminescent layer is configured to correspond to a peak electric field intensity 44, heightened luminescent effects are observed.

One aspect of the invention is to match the excitation wavelength of the luminescent material with the position of the luminescent layer in the stack. By placing the luminescent layer in the right position corresponding to a maximum electric field at the excitation wavelength of the luminescent layer, the efficiency of the luminescent emission is increased. Conversely, the thickness of the luminescent layer can be decreased through this optimum placement in the stack. This is advantageous because if the luminescent material has unwanted absorption, it would be advantageous to minimize the thickness of the luminescent layer in the stack.

The reflectance (and transmittance) spectra of thin film interference devices shifts to shorter wavelengths as the incident angle increases away from normal to the surface. The change in incident angle also shifts the electric field distribution within the thin film layers. Hence, the wavelength of maximum electric field intensity is a function of incident angle. Therefore, if the luminescent layer is placed at the electric field maximum at normal angle, then the intensity of the luminescent layer's absorption of the excitation energy should decrease with increasing angle making the device an angle-sensitive luminescent device. If instead the excitation wavelength is designed to be at a wavelength longer than that corresponding to the normal angle, then changing the angle will cause the absorption (and consequently the emission) intensity to start low, increase, then decrease again.

Thus, the multilayered structure shown in Figure 2 would have an increasing intensity with increasing angle, and the multilayered structure shown in Figure 3 would have a decreasing intensity with increasing angle.

Referring now to Figures 4-13, one skilled in the art will recognize, in view of the disclosure herein, that various luminescent materials as discussed above can be incorporated into the multilayered thin film structures discussed hereafter.

Figure 4 depicts alternative coating structures (with phantom lines) for a color-shifting pigment flake 50 in the form of an encapsulate according to other embodiments of the invention. The flake 50 has a core layer 52, which can be overcoated by an encapsulating dielectric layer 54 substantially surrounding the core layer 52. An absorber layer 56, which overcoats dielectric layer 54, provides an outer encapsulation of flake 50. The hemispherical lines on one side of the flake 50 indicate that dielectric layer 54 and absorber layer 56 can be formed as contiguous

layers.

Alternatively, core layer 52 and dielectric layer 54 can be in the form of a thin film core flake stack, in which opposing dielectric layers 54a, 54b are preformed on the top and bottom surfaces but not on at least one side surface of core layer 52, with the absorber layer 56 encapsulating the thin film stack. An encapsulation process can also be used to form additional layers on flake 50 such as a capping layer (not shown).

Various luminescent materials as discussed above can be incorporated into the multilayer structure of flake 50 by the methods of the invention. Suitable materials and thicknesses for the dielectric layer(s) and absorber layer of flake 50 are the same as taught hereinabove for corresponding layers of flake 20 in Figure 1. The core layer 52 can comprise a metallic reflector such as discussed above for reflector layer 22 of flake 20, as well as other materials such glass, silica, mica, indium-tin-oxide (ITO), needles, micropatterned particles, liquid crystal platelets, and the like.

In addition, core layer 52 can be a multi-layered core flake section structure, such as a "bright metal flake" as disclosed in U.S. Patent No. 6,013,370 to Coulter et al., and U.S. Application Serial No. 09/207,121, filed December 7, 1998, the disclosures of which are incorporated by reference herein. Such a multi-layered structure includes a reflector sublayer having a top surface, a bottom surface, and at least one side surface, and a support sublayer preformed on at least one of the top and bottom surfaces but not on the at least one side surface of the reflector sublayer. The reflector sublayer can be a metal such as aluminum having a thickness of at least about 40 nm, and the support layer(s) can be a dielectric such as silicon oxide having a thickness of at least about 10 nm, with the thickness being chosen so that the dielectric sublayers do not substantially affect the color properties of the reflector sublayer. For example, a multilayered core flake section can have the coating structure $SiO_x/Al/SiO_x$, where x is from about 1 to about 2.

The core layer 52 can also be a multi-layered structure such as a "composite reflective flake" as disclosed in copending U.S. Application Serial No. 09/626,041 to Coulter et al., filed July 27, 2000, the disclosure of which is incorporated by reference herein. Such a multi-layered structure includes a central support sublayer having a top surface, a bottom surface, and at least one side surface, and a reflector sublayer

preformed on one or both of the top and bottom surfaces but not on the at least one side surface of the reflector sublayer.

Figure 5 depicts another alternative coating structure for a color-shifting pigment flake 60 according to the present invention. The flake 60 includes a core layer 52 and a single dielectric layer 54, which extends over top and bottom surfaces of the core layer 52 to form a dielectric-coated preflake 62. The dielectric-coated preflake has two side surfaces 64 and 66. Although side surface 66 is homogeneous and formed only of the dielectric material of dielectric layer 54, side surface 64 has distinct surface regions of dielectric 64a, reflector 64b, and dielectric 64c, respectively. The dielectric-coated preflake is further coated on all sides with an absorber layer 56. The absorber layer is in contact with the dielectric layer 54 and core layer 52 at side surface 64. Various luminescent materials as described previously can be incorporated into the multilayer structure of flake 60 according to the methods of the invention.

The structure of the pigment flake 60 typically occurs because of a preflake coating process such as disclosed in U.S. Application Serial No. 09/512,116, filed on February 24, 2000, the disclosure of which is incorporated by reference herein. In such a process, one or more thin film layers including at least a core reflector layer are deposited on a web to form a film, which is subsequently fractured and removed from the web to form a plurality of pigment preflakes. The preflakes can be a dielectric-coated flake, in which a dielectric coating completely encapsulates a core flake section. The preflakes are broken into sized preflakes using any conventional fragmentation process, such as by grinding. The sized preflakes will include some sized preflakes having top and bottom dielectric layers with no dielectric material overcoating the side surfaces of the preflake, such as shown for one embodiment of flake 50 in Figure 4 in which the core layer is coated with top and bottom dielectric layers. Other sized preflakes will have a single dielectric layer extending over both top and bottom surfaces of the core flake section, leaving one side surface of the core flake section exposed, such as shown for dielectric-coated preflake 62 in Figure 5. Because of the fragmentation process, substantially all of the sized preflakes have at least a portion of a side surface exposed. The sized preflakes are then coated on all sides with an absorber layer, such as shown for flake 60 of Figure 5.

Figure 6 depicts another alternative coating structure for a color-shifting pigment flake 80 in the form of an encapsulate. The flake has a thin core layer 82, which can be formed of a particulate substrate material that provides rigidity, such as mica, glass flake, talc, or other silicatic material, as well as iron oxide, boron nitride, and the like. The core layer 82 is overcoated on all sides with a reflector coating 84, such as a reflective metallic coating, which can be composed of the same materials as described above for reflector layer 22 of flake 20. An encapsulating dielectric layer 54 substantially surrounds reflector coating 84. An absorber layer 56, which overcoats dielectric layer 54, provides an outer encapsulation of flake 80. Various luminescent materials as described previously can be incorporated into the multilayer structure of flake 80 according to the methods of the invention.

Various coating processes can be utilized in forming the dielectric and absorber coating layers by encapsulation. For example, suitable preferred methods for forming the dielectric layer include vacuum vapor deposition, sol-gel hydrolysis, CVD in a fluidized bed, and electrochemical deposition. A suitable SiO_2 sol-gel process is described in U.S. Patent No. 5,858,078 to Andes et al., the disclosure of which is incorporated by reference herein. Other examples of suitable sol-gel coating techniques useful in the present invention are disclosed in U.S. Patent No. 4,756,771 to Brodalla; Zink et al., *Optical Probes and Properties of Aluminosilicate Glasses Prepared by the Sol-Gel Method*, Polym. Mater. Sci. Eng., 61, pp. 204-208 (1989); and McKiernan et al., *Luminescence and Laser Action of Coumarin Dyes Doped in Silicate and Aluminosilicate Glasses Prepared by the Sol-Gel Technique*, J. Inorg. Organomet. Polym., 1(1), pp. 87-103 (1991); with the disclosures of each of these incorporated by reference herein.

Suitable preferred methods for forming the absorber layers include vacuum vapor deposition, and sputtering onto a mechanically vibrating bed of particles, such as disclosed in U.S. Application Serial No. 09/389,962, filed September 3, 1999, which is incorporated by reference herein. Alternatively, the absorber coating may be deposited by decomposition through pyrolysis of metal-organo compounds or related CVD processes which may be carried out in a fluidized bed as described in U.S. Patent Nos. 5,364,467 and 5,763,086 to Schmid et al., the disclosures of which are incorporated by reference herein. Another method of depositing the absorbers of the

invention is by plasma enhanced chemical vapor deposition (PECVD) where the chemical species are activated by a plasma. Such a method is disclosed in detail in U.S. Application Serial No. 09/685,468, filed on October 10, 2000, which is incorporated by reference herein.

If no further grinding is carried out, these encapsulation methods result in an encapsulated core flake section with dielectric and absorber materials therearound. Various combinations of the above coating processes may be utilized during manufacture of pigment flakes with multiple encapsulating coatings. When pigment flakes are formed by a sequential encapsulation process, it will be appreciated that each respective encapsulating layer is generally a continuous layer composed of one material and having substantially the same thickness around the flake structure.

There are various methods which can be utilized to incorporate a luminescent material or layer into a color-shifting flake formed by encapsulation processes. Including luminescent materials in a multilayered color-shifting particle is difficult because of the high temperatures required to process the luminescent materials and obtain the proper stoichiometry. The present invention provides various methods such that the stoichiometry problem can be overcome.

In one method, thin film seed particles are coated with luminescent precursors in a sol-gel or equivalent process, and then the particles are heated in the appropriate atmosphere in order to create the proper stoichiometry. For example, the luminescent material is first dissolved or suspended in a sol-gel precursor solution and absorbed into pores of the sol-gel coating or bound to the surface of the coating. The sol-gel solution is then deposited onto the surfaces of seed particles through methods known in the art, for example, by solution codeposition. Next, the seed particles are removed from the sol-gel solution. Finally, water and/or alcohol are removed from the sol-gel coating on the particles by heating.

Alternatively, another method involves using a nanoreactor to provide the luminescent material in a matrix. This is accomplished by first forming porous nanospheres from a sol-gel precursor solution. The nanospheres are then imbibed with a luminescent material. The luminescent-imbibed nanospheres are then deposited onto seed particles. Finally, the coated seed particles are separated from the precursor solution. This method allows for control of the thickness and

composition of the luminescent material.

In both of the above sol-gel methods, the seed particle can comprise a multilayer structure such as bright metal flake or preflake, or a monolithic structure. Further, these methods can be used to apply the luminescent material as a separate layer or as part of a reflector, dielectric, absorber, or other functional layer. The sol-gel methods have the advantage of economics and efficiency, as well as ease of process. They are compatible with fragile luminescent materials and allow for tailored materials with exact stoichiometries.

Further, these methods allow for ease in producing high luminescent material doping levels, and provide for durable luminescent layers because the sol-gel coating shields the luminescent materials. These methods also allow for ease of particle orientation control. The unique crystallography produced by these methods can lead to unique optical properties, and the unique refractive indices produced allow for control of absorption.

Figure 7 depicts a luminescent color-shifting pigment flake 100 according to another embodiment of the invention. The flake 100 is a multi-layer design having a generally symmetrical multilayer thin film stack structure on opposing sides of a reflector layer 102. Thus, first and second dielectric layers 104a, 104b are disposed respectively on opposing sides of reflector layer 102, and first and second absorber layers 106a, 106b are disposed respectively on each of the dielectric layers 104a, 104b. A third dielectric layer 108a is formed on the first absorber layer 106a, and a fourth dielectric layer 108b is formed on the second absorber layer 106b. A third absorber layer 110a is on the third dielectric layer 108a, and a fourth absorber layer 110b is on the fourth dielectric layer 108b. These layers of flake 100 can be formed by a web coating and flake removal process as described previously.

As shown in Figure 7, each dielectric and absorber layer pair forms a repeating period 112, 114, of dielectric/absorber (*e.g.*, layers 104a and 106a, and layers 108a and 110a). One or more additional periods of dielectric/absorber layers may be added to flake 100 to obtain a desired optical effect.

Figure 7 further shows an alternative coating structure (with phantom lines) for the luminescent color-shifting flake 100, in which one or more of the absorber layers and dielectric layers are coated around reflector layer 102 in an encapsulation

process. For example, when an encapsulation process is used to form an outer absorber layer, absorber layers 110a and 110b are formed as part of a continuous absorber coating layer 110 substantially surrounding the flake structure thereunder. Likewise, an encapsulation process can also be used in forming an underlying dielectric layer, such that dielectric layers 108a and 108b are formed as part of a continuous dielectric coating layer 108 substantially surrounding the flake structure thereunder. An encapsulation process can also be used in forming the other dielectric 104 and absorber 106 layers such that reflector layer 102 is encapsulated sequentially with alternating dielectric and absorber layers.

Thus, the pigment flake 100 may be embodied either as a multilayer thin film stack flake or a multilayer thin film encapsulated particle with one or more encapsulating layers therearound. Suitable materials and thicknesses for the absorber, dielectric, and reflector layers of flake 100 are the same as taught hereinabove for flake 20. Various luminescent materials as described previously can be incorporated into the multilayer structure of flake 100 according to the methods of the invention.

Figure 8 depicts a luminescent color-shifting pigment flake 120 according to another embodiment of the invention which does not use a reflector. The flake 120 is a three-layer design having a generally symmetrical multilayer thin film structure on opposing sides of a dielectric layer 122. Thus, first and second absorber layers 124a and 124b are formed on opposing major surfaces of dielectric layer 122. These layers of flake 120 can be formed by a web coating and flake removal process as described previously.

Figure 8 further depicts an alternative coating structure (with phantom lines) for the luminescent color-shifting flake 120, in which an absorber layer is coated around dielectric layer 122 in an encapsulation process. Accordingly, absorber layers 124a and 124b are formed as part of a continuous absorber coating layer 124 substantially surrounding dielectric layer 122.

Thus, the pigment flake 120 may be embodied either as a multilayer thin film stack flake or a multilayer thin film encapsulated particle. Suitable materials and thicknesses for the absorber and dielectric layers of flake are the same as taught hereinabove for flake 20. Various luminescent materials as described previously can be incorporated into the multilayer structure of flake 120 according to the methods of

the invention.

Figure 9 illustrates a pigment flake 130 according to a further embodiment of the present invention. Pigment flake 130 comprises a core layer 132 which is substantially encapsulated by a first absorber layer 134. The absorber layer 134 is in turn encapsulated by a dielectric layer 136, such as a layer of SiO_2 or high index TiO_2 formed by a sol-gel process.. A second absorber layer 138 encapsulates dielectric layer 136. Thus, pigment flake 130 is embodied as a multilayer thin film encapsulated particle. The core layer 132 is preferably a flat, transparent planar material such as mica, glass, silica, indium tin oxide (ITO), or other dielectric material, which gives strength to the flake. Suitable materials and thicknesses for the absorber layers of flake 130 are the same as taught hereinabove for flake 20. Various luminescent materials as described previously can be incorporated into the multilayer structure of flake 130 according to the methods of the invention.

Some flakes of the invention can be characterized as multilayer thin film interference structures in which layers lie in parallel planes such that the flakes have first and second parallel planar outer surfaces and an edge thickness perpendicular to the first and second parallel planar outer surfaces. Such flakes are produced to have an aspect ratio of at least about 2:1, and preferably about 5-15:1 with a narrow particle size distribution. The aspect ratio of the flakes is ascertained by taking the ratio of the longest planar dimension of the first and second outer surfaces to the edge thickness dimension of the flakes.

The luminescent color-shifting pigment flakes of the present invention can be interspersed within a pigment medium to produce a colorant material which can be applied to a wide variety of objects or papers. The pigment flakes added to a medium produces a predetermined optical response through radiation incident on a surface of the solidified medium. Suitable pigment media include various polymeric materials or organic binders such as acrylic melamine, urethanes, polyesters, vinyl resins, acrylates, methyl methacrylate, ABS resins, epoxies, styrenes, ink and paint formulations based on alkyd resins, and mixtures thereof. The luminescent color-shifting flakes combined with the pigment media produce a colorant material that can be used directly as a paint, ink, or moldable plastic material. The colorant material can also be utilized as an additive to conventional paint, ink, or plastic materials.

In addition, the luminescent color-shifting flakes can be optionally blended with various additive materials such as conventional pigment flakes, particles, or dyes of different hues, chroma and brightness to achieve the color characteristics desired. For example, the flakes can be mixed with other conventional pigments, either of the interference type or noninterference type, to produce a range of other colors. This preblended material can then be dispersed into a polymeric medium such as a paint, ink, plastic or other polymeric pigment vehicle for use in a conventional manner.

Examples of suitable additive materials that can be combined with the luminescent color-shifting flakes of the invention include non-color-shifting high chroma or high reflective platelets which produce unique color effects, such as $MgF_2/Al/MgF_2$ platelets or $SiO_2/Al/SiO_2$ platelets. Other suitable additives that can be mixed with the luminescent color-shifting flakes include lamellar pigments such as aluminum flakes, graphite flakes, glass flakes, iron oxide, boron nitride, mica flakes, interference based TiO_2 coated mica flakes, interference pigments based on multiple coated plate-like silicatic substrates, metal-dielectric or all-dielectric interference pigments, and the like; and non-lamellar pigments such as aluminum powder, carbon black, ultramarine blue, cobalt based pigments, organic pigments or dyes, rutile or spinel based inorganic pigments, naturally occurring pigments, inorganic pigments such as luminescent dioxide, talc, china clay, and the like; as well as various mixtures thereof. For example, pigments such as aluminum powder or carbon black can be added to control lightness and other color properties.

The luminescent color-shifting flakes of the present invention are particularly suited for use in applications where colorants of high chroma and durability are desired. By using the luminescent color-shifting flakes in a colorant material, high chroma durable paint or ink can be produced in which variable color effects are noticeable to the human eye. The luminescent color-shifting flakes of the invention have a wide range of color-shifting properties, including large shifts in chroma (degree of color purity) and also large shifts in hue (relative color) with a varying angle of view. Thus, an object colored with a paint containing the luminescent color-shifting flakes of the invention will change color depending upon variations in the viewing angle or the angle of the object relative to the viewing eye.

The luminescent color-shifting flakes of the invention can be easily and

economically utilized in paints and inks which can be applied to various objects or papers, such as motorized vehicles, currency and security documents, household appliances, architectural structures, flooring, fabrics, sporting goods, electronic packaging/housing, product packaging, etc. The luminescent color-shifting flakes can also be utilized in forming colored plastic materials, coating materials, extrusions, electrostatic coatings, glass, and ceramic materials.

Generally, the color-shifting foils of the invention have a nonsymmetrical thin film coating structure, which can correspond to the layer structures on one side of a core layer in any of the above described embodiments related to thin film stack flakes. For example, a foil can be formed with repeating dielectric/absorber periods on one side of a reflector layer such as shown for the flake in Figure 7. Various luminescent materials as described previously can be incorporated into the multilayer structure of the foils described as follows according to the methods of the invention. The foils can be laminated to various objects or can be formed on a carrier substrate.

Figure 10 depicts a coating structure of a luminescent color-shifting foil 200 formed on a substrate 202, which can be any suitable material such as a flexible PET web, carrier substrate, or other plastic material. A suitable thickness for substrate 202 is, for example, about 0.5 to about 7 mils. The foil 200 includes a reflector layer 204 on substrate 202, a dielectric layer 206 on reflector layer 204, and an absorber layer 208 on dielectric layer 206. The reflector, dielectric and absorber layers can be composed of the same materials and can have the same thicknesses as described above for the corresponding layers in flake 20.

The foil 200 can be formed by a web coating process, with the various layers as described above sequentially deposited on a web by conventional deposition techniques to form a thin film foil structure. The foil 200 can be formed on a release layer (not shown) of a web so that the foil can be subsequently removed and attached to a surface of an object. The foil 200 can also be formed on a carrier substrate 202, which can be a web without a release layer.

Figure 11 depicts a coating structure of a color-shifting foil 210 formed on a carrier substrate 212. The foil 210 includes a first absorber layer 214 on substrate 212, a dielectric layer 216 on absorber layer 214, and a second absorber layer 218 on dielectric layer 216, but does not include a reflector layer. Such a film structure

allows the foil to be transparent to light incident upon the surface thereof, thereby providing for visual verification or machine readability of information below foil 210 on carrier substrate 212. The dielectric and absorber layers of foil 210 can be composed of the same materials and can have the same thicknesses as described above for the corresponding layers in flake 20.

The foils of the invention can be used in a hot stamping configuration where the thin film stack of the foil is removed from the release layer of a substrate by use of a heat activated adhesive. The adhesive can be either coated on a surface of the foil opposite from the substrate, or can be applied in the form of a UV activated adhesive to the surface on which the foil will be affixed. Further details of making and using optical stacks as hot stamping foils can be found in U.S. Patent Nos. 5,648,165, 5,002,312, 4,930,866, 4,838,648, 4,779,898, and 4,705,300, the disclosures of which are incorporated by reference herein.

Figure 12 illustrates one embodiment of a foil 220 disposed on a web 222 having an optional release layer 224 on which is deposited a reflector layer 226, a dielectric layer 228, and an absorber layer 230. The foil 220 may be utilized attached to web 222 as a carrier when the release layer is not employed. Alternatively, foil 220 may be laminated to a transparent substrate (not shown) via an optional adhesive layer 232, such as a transparent adhesive or ultraviolet (UV) curable adhesive, when the release layer is used. The adhesive layer 232 can be applied to absorber layer 230 or the transparent substrate.

Figure 13 depicts an alternative embodiment in which a foil 240 having the same thin film layers as foil 220 discussed above is disposed on a web 222 having an optional release layer 224. The foil 240 is formed such that absorber layer 230 is deposited on web 222. The foil 240 may be utilized attached to web 222 as a carrier, which is preferably transparent, when the release layer is not employed. The foil 240 may also be attached to a substrate (not shown) when release layer 224 is used, via an adhesive layer 242 such as a hot stampable adhesive, a pressure sensitive adhesive, a permanent adhesive, and the like. The adhesive layer 242 is applied to reflector layer 226 or can be applied to the substrate.

As discussed hereinabove, it is desirable to add additional covert features to color-shifting devices. Accordingly, it has been advantageously discovered that the

luminescent color-shifting pigments of the present invention can effectively be used in a mixture with distinct luminescent color-shifting pigments or non-luminescent color-shifting pigments in varying predetermined ratios to add covert features to color-shifting pigment compositions. The covert feature provides a particular advantage in packaging and sales of the color-shifting pigments to customers because the covert feature allows the manufacturer to track their products based upon the customer to whom it is sold.

Thus, a luminescent color-shifting pigment can comprise a mixture of color-shifting pigments and luminescent color-shifting pigments. For example, a product with a preferred color shift can be sold in a mixture of about 80% of the color-shifting pigment and about 20% of the luminescent color-shifting pigment to one customer. Another product could be sold to a different customer with about 60% of the non-luminescent color-shifting pigment and about 40% of the luminescent color-shifting pigment. Although the pigments will have virtually identical color-shifting features, the differing percentages of luminescent pigments will create two products with differing magnitudes of luminescence as a covert feature. Therefore, while only manufacturing two color-shifting pigment products that have the same color shift (one luminescent), a variety of distinguishable color-shifting devices can be produced by varying the ratio of the two pigments in the mixture to produce color-shifting compositions that have varying predetermined degrees of luminescence.

Accordingly, another embodiment of the invention is directed to a colorant composition which includes luminescent and non-luminescent color shifting pigment flakes mixed in a predetermined ratio and dispersed in a pigment medium. In one preferred embodiment, the luminescent and non-luminescent color-shifting pigment flakes are combined in a mixture comprising at least about 1 wt-% luminescent color-shifting pigment flakes prior to dispersing in a pigment medium. In a more preferred embodiment, the luminescent and non-luminescent color-shifting pigment flakes are combined in a mixture comprising at least about 10 wt-% luminescent color-shifting pigment flakes prior to dispersing in a pigment medium.

Because the varying percentages of luminescent color-shifting pigment is measurable, a manufacturer or distributor of the product can track the use of the product they have sold to individual customers to insure compliance with sales

contracts. The covert feature can also be used in anti-counterfeiting measures for various products and documents. The covert feature allows the manufacture of the luminescent and non-luminescent color-shifting pigments to distinguish individual colorant compositions even though they may be indistinguishable to those unaware of the covert feature.

Of course one skilled in the art will recognize, in light of the disclosure herein, that multiple varieties of non-luminescent and luminescent color-shifting flakes may be combined to vary and increase the number of covert features in the ink. Thus, two or more distinct luminescent color-shifting pigments can be combined in a mixture with a non-luminescent color-shifting pigment. All of the pigments can have the same color shift with different luminescence effects. This approach provides the ability to create unique luminescent signatures by mixing color-shifting pigments. For example, one could mix 60% of a non-luminescent pigment, 30% of a luminescent pigment type A, and 10% of a luminescent pigment type B, with the resulting admixture having a characteristic luminescent signature that was the average of 30% A and 10% B while still having the desired overt color-shifting performance. To obtain a new luminescent signature, one could simply vary the ratio of type A to type B rather than synthesize new pigments.

Another way to distinguish pigments with the same color shift is to have varying depths of luminescent layers within the multilayer structure of the pigments, thus creating pigments with differing angle sensitive luminescence and providing yet another layer of covert security. For example, one luminescent pigment may be designed to have a maximum luminescence under light incident at 45° to normal while an otherwise identical pigment could be designed to have a maximum luminescence under light incident at 60° to normal.

The present invention provides numerous advantages and benefits. Primarily, the present invention provides pigment or foil components for security devices which have distinct and pronounced overt and covert features under visible wavelength and non-visible wavelength light sources. These distinct features are not easily duplicated and cannot be copied by simple mixtures of interference pigments and luminescent materials. Another advantage is that the covert features are machine readable, yet coexist with overt features such as the color-shifting nature of the materials. Thus,

although it may be apparent that security features exist, it is not apparent how many security features are present. Further, the covert features can selectively code additional information.

The luminescence feature adds to the value of color-shifting pigment products by potentially increasing thermal stability, mechanical stability, and durability. This feature also provides light fastness, as well as solvent and moisture resistance. Additionally, polarization control can be achieved by both the control of luminescent material orientation in the flake and the control of flake orientation in a resin or coating composition. The luminescence feature also provides advantages with regard to its spectral rectifying effects, such as angularly dependent luminescence or wavelength selective quenching.

Incorporating luminescent materials into multilayer flakes also has advantages over mixtures of luminescent particles and color-shifting flakes as to the shape of the luminescent materials. These advantages principally go to the "lay down" of the flakes. In other words, the geometric positioning of the luminescent material in a flake is flat, allowing for uniform positioning and thus uniform orientation of the luminescent flakes. Also, the inherent shape of the flake can be used to control the morphology of a luminescent layer in the flake and thereby provide for new optics.

The following examples are given to illustrate the present invention, and are not intended to limit the scope of the invention.

EXAMPLE 1

Figure 14 is a graph illustrating the way in which absorption varies in a luminescent color-shifting thin film stack by angle of incidence, and the characteristic absorption of a luminescent material at 520 nm. The reflectance of a luminescent thin film stack is plotted against the incident wavelength. Three separate hypothetical absorption curves 300, 302, and 304 for light incident respectively at 45°, 0°, and 60° from normal are plotted. A reflector/dielectric/absorber coating structure having nominal gold-to-green color shift, with a luminescent material placed within the dielectric layer, is hypothetically considered. In this example, the luminescent material placed within the dielectric layer absorbs at 520 nm and re-emits at 720 nm. This difference in wavelength between the apex of the absorption and emission spectrums is called the Stokes shift.

The notch 306 in the 45° curve illustrates the characteristic absorption of the luminescent material at 520 nm. As can be seen, the 45° incident light will be absorbed by the luminescent material and reemitted at 720 nm, while light incident at 60° or 0° will generally not be absorbed by the luminescent material. Such a characteristic allows a luminescent material to be selected to emit outside of observation wavelengths while absorbing within the observation wavelengths. This creates an effect in which there are absorption bands detected at certain angles but not others, providing a covert taggant detectable in the spectrum.

EXAMPLE 2

Figure 15 is a graph illustrating the angle-sensitive emission 320 of a luminescent color-shifting pigment according to the invention. The graph illustrates how changes in the incident angle of electromagnetic energy results in different emission levels. As shown, there exists a peak 322 of maximum absorption that corresponds to a particular wavelength. Thus, a given luminescent will highly absorb at one angle of incidence but not at others. This feature of the invention allows for further customization and differentiation of luminescent color-shifting pigments and foils.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A luminescent color-shifting pigment flake, comprising:

a reflector layer;

a first dielectric layer overlying the reflector layer;

a first absorber layer overlying the first dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

2. The pigment flake of claim 1, further comprising a second dielectric layer overlying the reflector layer opposite from the first dielectric layer.

3. The pigment flake of claim 2, further comprising a second absorber layer overlying the second dielectric layer opposite from the first absorber layer.

4. The pigment flake of claim 1, wherein the absorber layer substantially surrounds the dielectric layer and the reflector layer, and the dielectric layer substantially surrounds the reflector layer.

5. The pigment flake of claim 2, wherein the absorber layer substantially surrounds the first and second dielectric layers and the reflector layer.

6. The pigment flake of claim 1, wherein the reflector layer comprises a reflective material selected from the group consisting of aluminum, silver, copper, gold, platinum, tin, titanium, palladium, nickel, cobalt, rhodium, niobium, chromium, and combinations or alloys thereof.

7. The pigment flake of claim 1, wherein the reflector layer has a physical thickness of about 200 Å to about 10,000 Å.

8. The pigment flake of claim 1, wherein the reflector layer comprises a core flake section including a reflector sublayer having a top surface, a bottom surface, and at least one side surface, and a support sublayer preformed on at least one of the top and bottom surfaces but not on the at least one side surface of the reflector sublayer.

9. The pigment flake of claim 1, wherein the reflector layer comprises a composite reflective flake including a central support sublayer having a top surface, a bottom surface, and at least one side surface, and a reflector sublayer preformed on each of the top and bottom surfaces but not on the at least one side surface of the

reflector sublayer.

10. The pigment flake of claim 2, wherein the first and second dielectric layers comprise a dielectric material having an index of refraction of about 1.65 or less.

11. The pigment flake of claim 10, wherein the dielectric material is selected from the group consisting of silicon dioxide, aluminum oxide, magnesium fluoride, aluminum fluoride, cerium fluoride, lanthanum fluoride, neodymium fluoride, samarium fluoride, barium fluoride, calcium fluoride, lithium fluoride, and combinations thereof.

12. The pigment flake of claim 2, wherein the first and second dielectric layers comprise a dielectric material having an index of refraction of greater than about 1.65.

13. The pigment flake of claim 12, wherein the dielectric material is selected from the group consisting of zinc sulfide, zinc oxide, zirconium oxide, titanium dioxide, carbon, indium oxide, indium-tin-oxide, tantalum pentoxide, cerium oxide, yttrium oxide, europium oxide, iron oxides, hafnium nitride, hafnium carbide, hafnium oxide, lanthanum oxide, magnesium oxide, neodymium oxide, praseodymium oxide, samarium oxide, antimony trioxide, silicon carbide, silicon nitride, silicon monoxide, selenium trioxide, tin oxide, tungsten trioxide, and combinations thereof.

14. The pigment flake of claim 2, wherein the first and second dielectric layers have an optical thickness in a range from about 2 QWOT at a design wavelength of about 400 nm to about 9 QWOT at a design wavelength of about 700 nm.

15. The pigment flake of claim 2, wherein the first and second dielectric layers have the same optical thickness.

16. The pigment flake of claim 2, wherein the first and second dielectric layers are composed of the same material.

17. The pigment flake of claim 2, wherein the first and second dielectric layers are each composed of a dielectric optical stack having a plurality of alternating layers of a high index material and a low index material.

18. The pigment flake of claim 17, wherein the dielectric optical stack has

a gradient index of refraction.

19. The pigment flake of claim 2, wherein the first and second dielectric layers are each composed of a mixture or multiple sublayers of dielectric materials selected from the group consisting of low index materials, high index materials, and combinations thereof.

20. The pigment flake of claim 3, wherein the first and second absorber layers comprise an absorbing material selected from the group consisting of chromium, nickel, aluminum, palladium, platinum, titanium, vanadium, cobalt, iron, tin, tungsten, molybdenum, rhodium, niobium, carbon, graphite, silicon, germanium, and compounds, mixtures, or alloys thereof.

21. The pigment flake of claim 3, wherein the first and second absorber layers comprise a material selected from the group consisting of elemental titanium, titanium-based compounds, titanium-based alloys, and combinations thereof.

22. The pigment flake of claim 3, wherein the first and second absorber layers each have a physical thickness of about 30 Å to about 300 Å.

23. The pigment flake of claim 3, wherein the first and second absorber layers have the same physical thickness.

24. The pigment flake of claim 3, wherein the first and second absorber layers are composed of the same material.

25. The pigment flake of claim 1, wherein the luminescent material is excited by one or more energy sources selected from the group consisting of infrared radiation, ultraviolet radiation, visible light, electric fields, magnetic fields, and chemical reaction.

26. The pigment flake of claim 1, wherein the luminescent material exhibits fluorescence, phosphorescence, polarization, or non-linear optical effects.

27. The pigment flake of claim 1, wherein the luminescent material comprises a fluorescent dye combined with a liquid crystal polymer.

28. The pigment flake of claim 1, wherein the luminescent material comprises a crystalline phosphor material.

29. The pigment flake of claim 1, wherein the luminescent material comprises solid phase or water-soluble quantum dot particles.

30. The pigment flake of claim 1, wherein the luminescent material is

incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

31. The pigment flake of claim 1, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

32. A luminescent color-shifting pigment material comprising a plurality of color-shifting pigment flakes, the pigment flakes having a multilayer structure as defined in claim 1.

33. A luminescent color-shifting colorant composition, comprising:

a pigment medium; and

a plurality of luminescent color-shifting pigment flakes dispersed in the pigment medium, the pigment flakes having a multilayer structure as defined in claim 1.

34. The colorant composition of claim 33, wherein the pigment medium comprises a material selected from the group consisting of acrylic melamine, urethanes, polyesters, vinyl resins, acrylates, methyl methacrylate, ABS resins, epoxies, styrenes, ink and paint formulations based on alkyd resins, and mixtures thereof.

35. The colorant composition of claim 33, wherein the pigment flakes have a dimension on any surface thereof ranging from about 2 microns to about 200 microns.

36. The colorant composition of claim 33, further comprising a plurality of non-luminescent color-shifting pigment flakes dispersed in the pigment medium.

37. The colorant composition of claim 36, wherein the non-luminescent color-shifting pigment flakes and the luminescent color-shifting pigment flakes are combined in a predetermined ratio.

38. The colorant composition of claim 36, wherein the plurality of luminescent color-shifting pigment flakes include two or more luminescent flake types having the same color shift and combined in a predetermined ratio to produce a selected luminescent signature for the colorant composition.

39. A luminescent color-shifting pigment flake, comprising:

a first absorber layer;

a first dielectric layer overlying the first absorber layer;

a reflector layer overlying the first dielectric layer;

a second dielectric layer overlying the reflector layer;

a second absorber layer overlying the second dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

40. The pigment flake of claim 39, further comprising a third dielectric layer overlying the second absorber layer, and a fourth dielectric layer underlying the first absorber layer.

41. The pigment flake of claim 40, wherein the third and fourth dielectric layers form a continuous coating layer around the layers interior thereto.

42. The pigment flake of claim 40, further comprising a third absorber layer overlying the third dielectric layer, and a fourth absorber layer overlying the fourth dielectric layer.

43. The pigment flake of claim 42, wherein the third and fourth absorber layers form a continuous coating layer around the layers interior thereto.

44. The pigment flake of claim 42, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

45. The pigment flake of claim 39, wherein at least one of the first dielectric layer and the second dielectric layer is composed partially or wholly of the luminescent material.

46. The pigment flake of claim 39, wherein at least one of the first absorber layer and the second absorber layer is composed partially or wholly of the luminescent material.

47. The pigment flake of claim 39, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å .

48. A luminescent color-shifting pigment flake, comprising:

a core layer;

a dielectric layer substantially surrounding the core layer;

an absorber layer substantially surrounding the dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

49. The pigment flake of claim 48, further comprising at least one additional dielectric layer and at least one additional absorber layer which substantially surround the other layers of the pigment flake.

50. The pigment flake of claim 48, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

51. The pigment flake of claim 48, wherein the dielectric layer is composed partially or wholly of the luminescent material.

52. The pigment flake of claim 48, wherein the absorber layer is composed partially or wholly of the luminescent material.

53. The pigment flake of claim 48, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

54. A luminescent color-shifting pigment flake, comprising:

a core reflector layer having a top surface, a bottom surface, and at least one side surface;

a dielectric layer overlying the top surface and the bottom surface but not on at least one side surface of the reflector layer;

an absorber layer substantially surrounding the dielectric layer and in contact with at least one side surface of the reflector layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

55. The pigment flake of claim 54, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at

excitation wavelengths enters the pigment flake.

56. The pigment flake of claim 54, wherein the dielectric layer is composed partially or wholly of the luminescent material.

57. The pigment flake of claim 54, wherein the absorber layer is composed partially or wholly of the luminescent material.

58. The pigment flake of claim 54, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

59. A luminescent color-shifting pigment flake, comprising:

a core layer;

a reflector coating substantially surrounding the core layer;

a dielectric layer substantially surrounding the reflector coating;

an absorber layer substantially surrounding the dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

60. The pigment flake of claim 59, wherein the core layer comprises a material selected from the group consisting of mica, glass, talc, iron oxide, and boron nitride.

61. The pigment flake of claim 59, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

62. The pigment flake of claim 59, wherein the dielectric layer is composed partially or wholly of the luminescent material.

63. The pigment flake of claim 59, wherein the absorber layer is composed partially or wholly of the luminescent material.

64. The pigment flake of claim 59, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

65. A luminescent color-shifting pigment flake, comprising:

a core layer;

a first absorber layer substantially surrounding the core layer;

a dielectric layer substantially surrounding the first absorber layer;

a second absorber layer substantially surrounding the dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

66. The pigment flake of claim 65, wherein the core layer is composed of mica or glass.

67. The pigment flake of claim 65, wherein the dielectric layer is composed of silicon dioxide or titanium dioxide.

68. The pigment flake of claim 67, wherein the dielectric layer is formed by a sol-gel process

69. The pigment flake of claim 65, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

70. The pigment flake of claim 65, wherein the dielectric layer includes the luminescent material.

71. The pigment flake of claim 65, wherein at least one of the first and second absorber layers is composed partially or wholly of the luminescent material.

72. The pigment flake of claim 65, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

73. A luminescent color-shifting pigment flake, comprising:

a first absorber layer;

a dielectric layer overlying the first absorber layer;

a second absorber layer overlying the dielectric layer; and

at least one luminescent material incorporated into the pigment flake;

wherein the pigment flake exhibits a discrete color shift such that the pigment flake has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

74. The pigment flake of claim 73, wherein the pigment flake exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the pigment flake.

75. The pigment flake of claim 73, wherein the dielectric layer includes the luminescent material.

76. The pigment flake of claim 73, wherein at least one of the first and second absorber layers is composed partially or wholly of the luminescent material.

77. The pigment flake of claim 73, wherein the luminescent material is incorporated into the flake as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

78. The pigment flake of claim 73, wherein the first and second absorber layers form a continuous coating layer that encapsulates the dielectric layer.

79. A luminescent color-shifting foil, comprising:

a reflector layer;

a dielectric layer overlying the reflector layer;

an absorber layer overlying the dielectric layer; and

one or more luminescent materials incorporated into the foil;

wherein the foil exhibits a discrete color shift such that the foil has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

80. The foil of claim 79, further comprising an adhesive layer for laminating the foil to a substrate.

81. The foil of claim 80, wherein the adhesive layer is selected from the group consisting of a hot stampable adhesive, a pressure sensitive adhesive, a permanent adhesive, a transparent adhesive, and a UV curable adhesive.

82. The foil of claim 79, wherein the luminescent materials are excited by one or more energy sources selected from the group consisting of infrared radiation, ultraviolet radiation, visible light, electric fields, magnetic fields, and chemical reaction.

83. The foil of claim 79, wherein the luminescent materials exhibit fluorescence, phosphorescence, polarization, or non-linear optical effects.

84. The foil of claim 79, wherein the luminescent materials are composed

of solid phase or water-soluble quantum dot particles.

85. The foil of claim 79, wherein the foil exhibits a luminescence intensity that is dependent upon the angle at which incident light at excitation wavelengths enters the foil.

86. The foil of claim 79, wherein the dielectric layer includes a luminescent material.

87. The foil of claim 79, wherein the absorber layer includes a luminescent material.

88. The foil of claim 79, wherein the luminescent material is incorporated into the foil as a distinct luminescent layer having a physical thickness of about 50 Å to about 15,000 Å.

89. A color-shifting foil device, comprising:

a carrier substrate;

a first absorber layer overlying the carrier substrate;

a dielectric layer overlying the first absorber layer;

a second absorber layer overlying the dielectric layer; and

one or more luminescent materials incorporated into the foil;

wherein the foil exhibits a discrete color shift such that the foil has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing.

90. A method of fabricating a luminescent pigment flake or foil material that exhibits a discrete color shift such that the material has a first color at a first angle of incident light or viewing and a second color different from the first color at a second angle of incident light or viewing, the method comprising:

providing one or more reflector layers;

forming one or more dielectric layers over the reflector layers;

forming one or more absorber layers over the dielectric layers; and

incorporating a luminescent material into the flake or foil as a separate layer or as at least part of one or more of the reflector layer, dielectric layer, or absorber layer.

91. The method of claim 90, wherein the dielectric and absorber layers are

formed by a process selected from the group consisting of physical vapor deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, sputtering, and electrolysis deposition.

92. The method of claim 90, wherein the luminescent material is excited by one or more energy sources selected from the group consisting of infrared radiation, ultraviolet radiation, visible light, electric fields, magnetic fields, and chemical reaction.

93. The method of claim 90, wherein the luminescent material exhibits fluorescence, phosphorescence, polarization, or non-linear optical effects.

94. The method of claim 90, wherein the luminescent material comprises solid phase or water-soluble quantum dot particles.

95. The method of claim 90, wherein the luminescent material is incorporated into the flake or foil by a sol-gel process.

96. The method of claim 90, wherein the luminescent material is dissolved in a sol-gel precursor solution prior to being incorporated into the flake or foil.

97. The method of claim 95, wherein the sol-gel process comprises:

forming porous nanospheres from a sol-gel precursor solution;

imbibing the nanospheres with a luminescent material; and

depositing the luminescent-imbibed nanospheres onto one or more of the layers, or to form at least part of one or more of the layers in the flake or foil material.

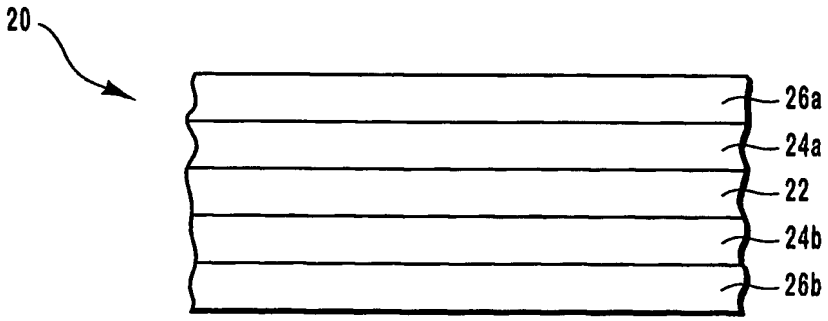

Fig. 1

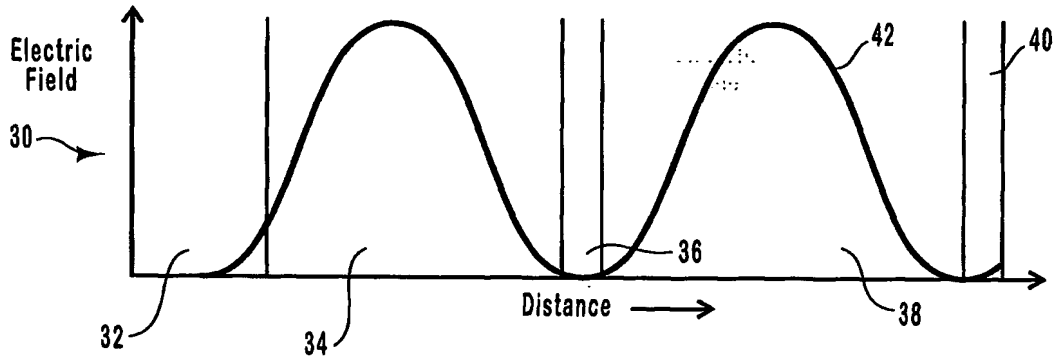

Fig. 2

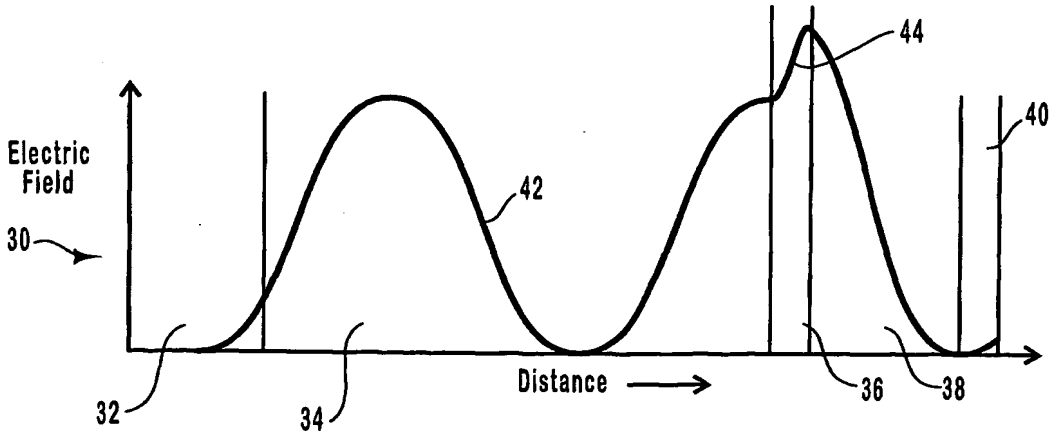

Fig. 3

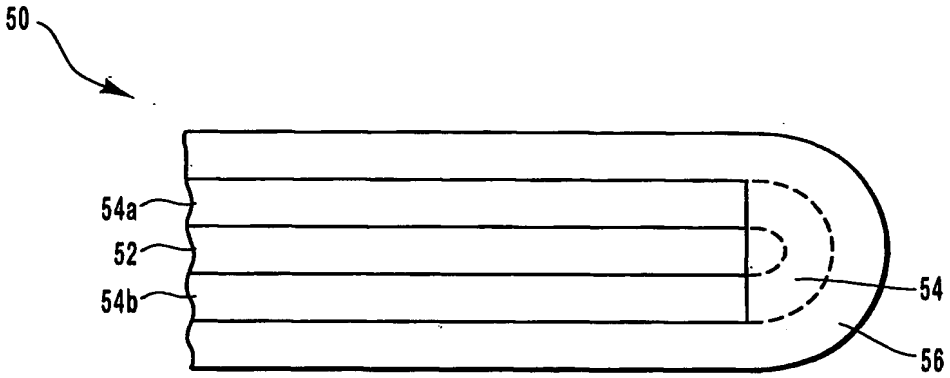

Fig. 4

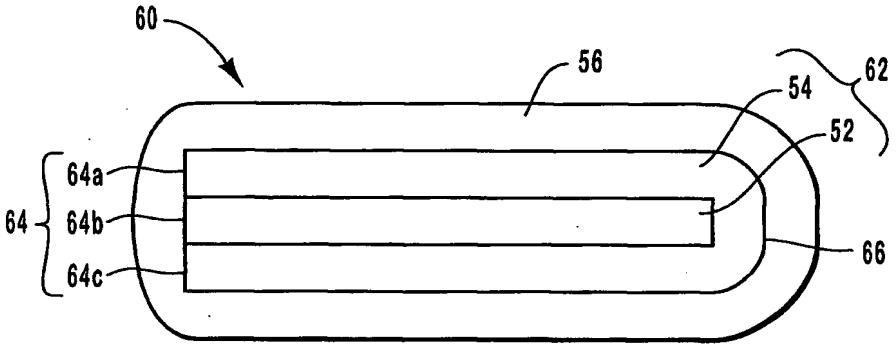

Fig. 5

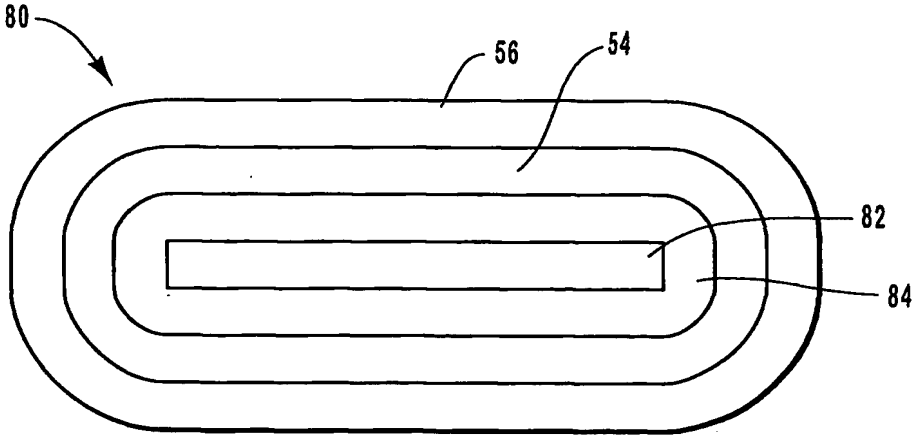

Fig. 6

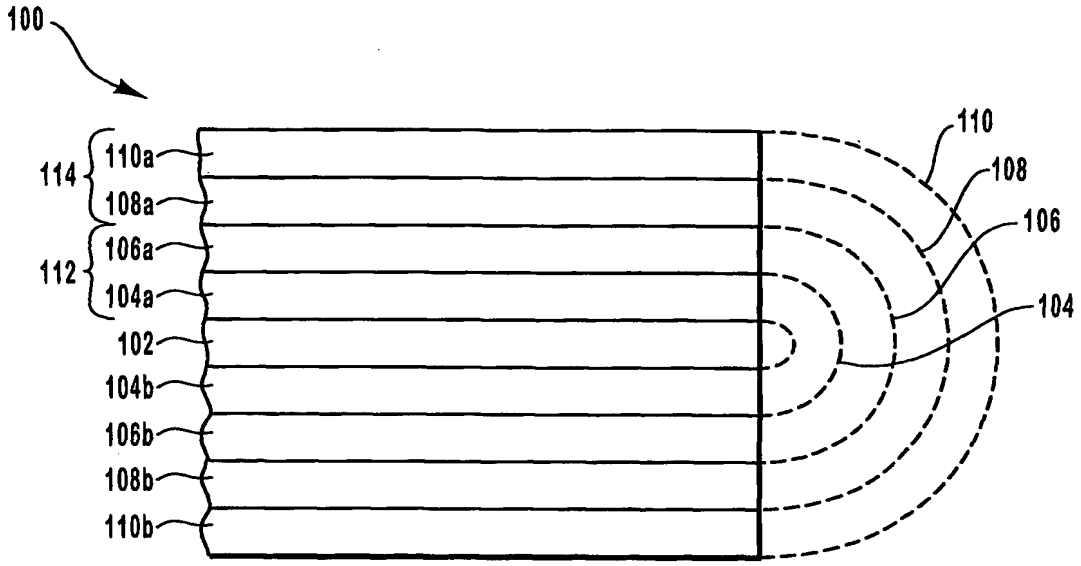

Fig. 7

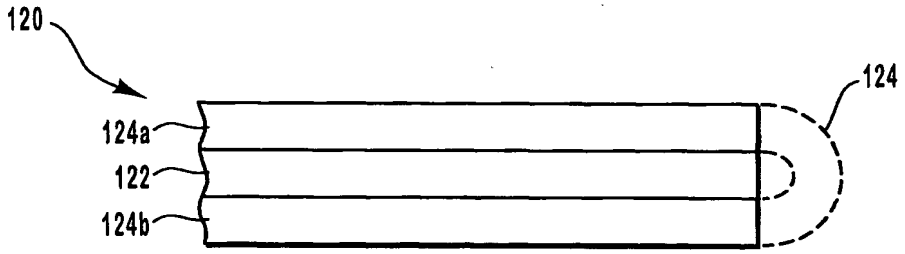

Fig. 8

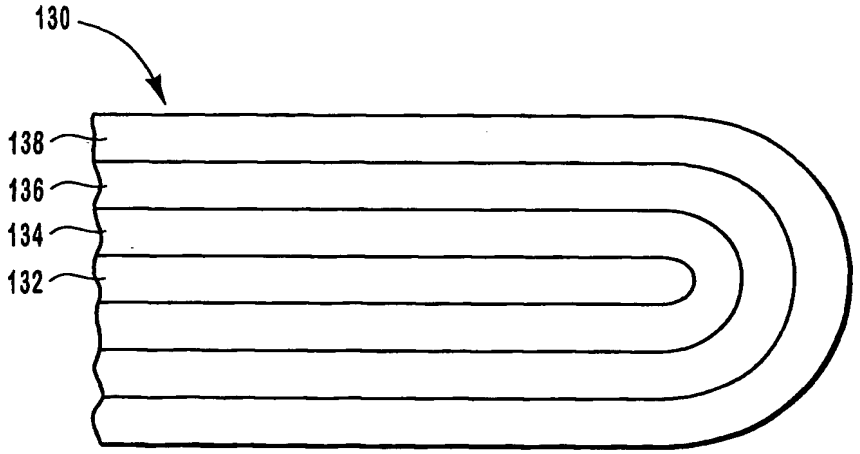

Fig. 9

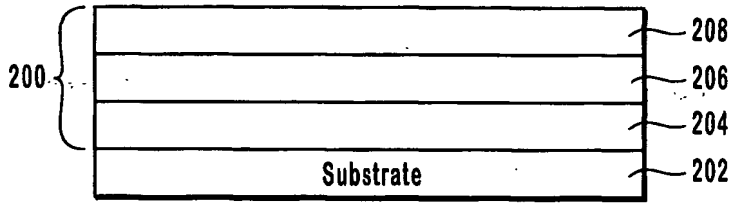

Fig. 10

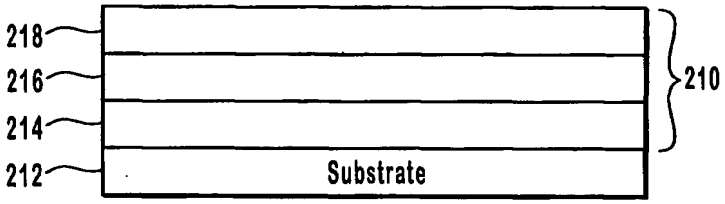

Fig. 11

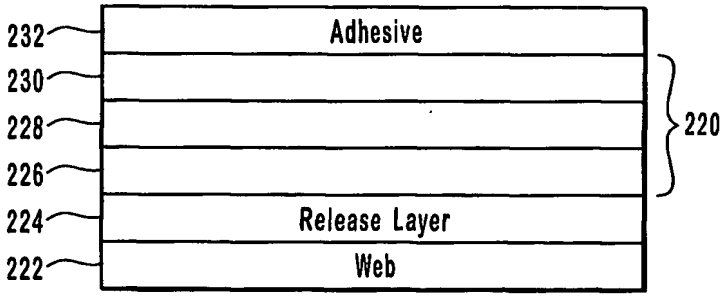

Fig. 12

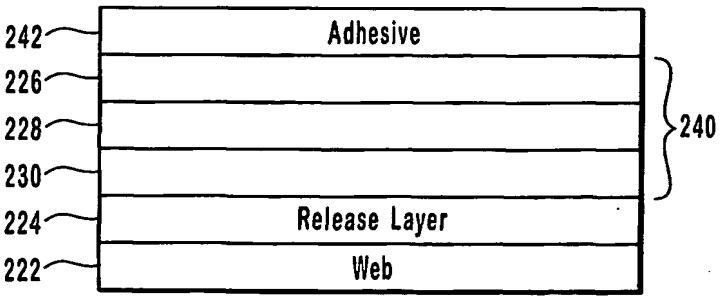

Fig. 13

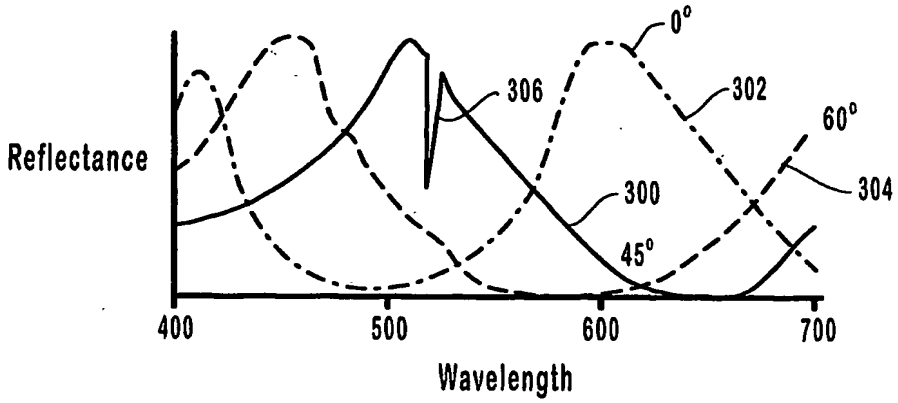
Reflectance
0°
306
302
60°
304
300
45°
400
500
600
700
Wavelength

Fig. 14

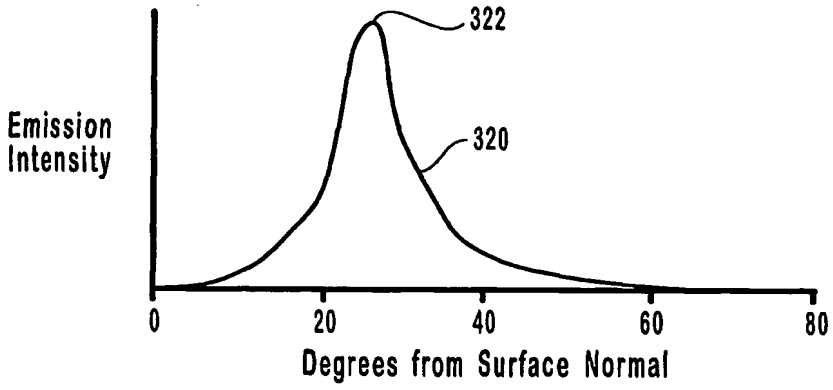
Emission Intensity
322
320
0
20
40
60
80
Degrees from Surface Normal

Fig. 15

INTERNATIONAL SEARCH REPORT

Inte ial Application No
PCT/US 01/20899

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, INSPEC, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 41 253 A (BASF) 8 March 2001 (2001-03-08) page 2, line 46 - line 61; claims 1-10 page 3, line 31 - line 37 page 4, line 9 page 4, line 24 page 5, line 59 -page 6, line 8 page 6, line 38 - line 41	1,6,11, 13,20, 25,33
X	US 5 571 624 A (R W PHILIPS) 5 November 1996 (1996-11-05) column 6, line 1 - line 18; claims 1-5; figure 6	1-3,6, 11,13, 15,16, 20,24, 33,34, 39,45

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 January 2002	06/02/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Vanhecke, H

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INTERNATIONAL SEARCH REPORT

Inter . ial Application No
PCT/US 01/20899

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 150 022 A (K E COULTER) 21 November 2000 (2000-11-21) column 10, line 41; claims 1-72; figures 1-4B column 5, line 44 -column 11, line 67	1-97
X	WO 00 31571 A (FLEX) 2 June 2000 (2000-06-02) page 4, line 19 -page 9, line 20; claims 1-49; figure 1 page 5, line 31	1-97
X	US 5 281 480 A (R W PHILIPS) 25 January 1994 (1994-01-25) column 7, line 59 -column 10, line 41; claims 1,2; figures 3A-3B column 7, line 68 -column 8, line 3	1
A	EP 0 927 749 A (SICPA) 7 July 1999 (1999-07-07) claims 1,9-14	1
A	US 5 766 335 A (P BUJARD) 16 June 1998 (1998-06-16) column 5, line 54 - line 63; claims 1-36	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte nal Application No
PCT/US 01/20899

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 19941253	A	08-03-2001	DE	19941253 A1	08-03-2001
			WO	0116236 A1	08-03-2001
US 5571624	A	05-11-1996	US	5569535 A	29-10-1996
			US	5648165 A	15-07-1997
			US	5279657 A	18-01-1994
			US	5171363 A	15-12-1992
			US	5059245 A	22-10-1991
			US	4434010 A	28-02-1984
			BR	9507492 A	12-08-1997
			CA	2188156 A1	02-11-1995
			DE	784601 T1	02-01-1998
			EP	0784601 A1	23-07-1997
			ES	2109202 T1	16-01-1998
			GR	97300030 T1	30-09-1997
			JP	3056253 B2	26-06-2000
			JP	9508172 T	19-08-1997
			WO	9529140 A1	02-11-1995
			US	5570847 A	05-11-1996
			US	5766738 A	16-06-1998
			US	5383995 A	24-01-1995
			US	5084351 A	28-01-1992
			US	5653792 A	05-08-1997
			US	5135812 A	04-08-1992
			US	5281480 A	25-01-1994
			AT	76888 T	15-06-1992
			AU	606321 B2	07-02-1991
			AU	6645186 A	25-06-1987
			AU	637900 B2	10-06-1993
			AU	7611391 A	08-08-1991
			CA	1315448 A1	30-03-1993
			CA	1329733 A1	24-05-1994
			DE	3685566 D1	09-07-1992
			DE	3685566 T2	24-12-1992
			DK	36695 A	03-04-1995
			DK	128393 A	12-11-1993
			DK	628586 A	24-06-1987
			EP	0227423 A2	01-07-1987
			ES	2031454 T3	16-12-1992
			GR	3005337 T3	24-05-1993
			JP	1658351 C	21-04-1992
			JP	3022427 B	26-03-1991
			JP	62260875 A	13-11-1987
			NZ	218573 A	28-11-1989
US 6150022	A	21-11-2000	EP	1141143 A1	10-10-2001
			WO	0034395 A1	15-06-2000
WO 0031571	A	02-06-2000	US	6157489 A	05-12-2000
			CN	1313953 T	19-09-2001
			EP	1133706 A1	19-09-2001
			WO	0031571 A1	02-06-2000
			US	6243204 B1	05-06-2001
			US	6246523 B1	12-06-2001
			US	6236510 B1	22-05-2001
US 5281480	A	25-01-1994	US	5059245 A	22-10-1991
			US	4434010 A	28-02-1984

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int[illegible]nal Application No
PCT/US 01/20899

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5281480 A		US	5135812 A	04-08-1992
		US	5383995 A	24-01-1995
		US	5648165 A	15-07-1997
		US	5569535 A	29-10-1996
		US	5084351 A	28-01-1992
		US	5653792 A	05-08-1997
		US	5570847 A	05-11-1996
		US	5571624 A	05-11-1996
		US	5766738 A	16-06-1998
		US	5171363 A	15-12-1992
		US	5279657 A	18-01-1994
		AT	76888 T	15-06-1992
		AU	606321 B2	07-02-1991
		AU	6645186 A	25-06-1987
		AU	637900 B2	10-06-1993
		AU	7611391 A	08-08-1991
		CA	1315448 A1	30-03-1993
		CA	1329733 A1	24-05-1994
		DE	3685566 D1	09-07-1992
		DE	3685566 T2	24-12-1992
		DK	36695 A	03-04-1995
		DK	128393 A	12-11-1993
		DK	628586 A	24-06-1987
		EP	0227423 A2	01-07-1987
		ES	2031454 T3	16-12-1992
		GR	3005337 T3	24-05-1993
		JP	1658351 C	21-04-1992
		JP	3022427 B	26-03-1991
		JP	62260875 A	13-11-1987
		NZ	218573 A	28-11-1989
EP 927749 A	07-07-1999	EP	0927749 A1	07-07-1999
		AU	2276199 A	19-07-1999
		CN	1283216 T	07-02-2001
		WO	9934315 A2	08-07-1999
		EP	0927750 A1	07-07-1999
		HU	0100329 A2	28-06-2001
		NO	20003385 A	17-08-2000
		PL	342101 A1	21-05-2001
		TR	200001875 T2	22-01-2001
		US	6200628 B1	13-03-2001
US 5766335 A	16-06-1998	CA	2203585 A1	25-10-1997
		EP	0803549 A2	29-10-1997
		JP	10060303 A	03-03-1998
		DE	59704636 D1	25-10-2001